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PRODUCTION OF IRON- AND SILICON-DOPED MAX PHASES BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

V. A. Martirosyan[1], M. E. Sasuntsyan[1], N. G. Saakyan[1], A. A. Frangulyan[1]

[1] *National Polytechnic University of Armenia (Erevan, Armenia)*

E-mail: v.a.martirosyan@mail.ru; msasuntsyan@mail.ru; nina.saakyan@mail.ru; albertaranea@mail.ru

AUTHOR'S INFO

V. A. Martirosyan, Dr. Eng., Prof., Dept. of General Chemistry and Chemical Processes,
M. E. Sasuntsyan, Cand. Eng., Associate Prof., Dept. of General Chemistry and Chemical Processes,
N. G. Saakyan, Post-graduate, Faculty of Metallurgy and Mineral Development,
A. A. Frangulyan, Cand. Eng., Head of the Faculty of Metallurgy and Mineral Development

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ABSTRACT

This paper looks at the possibility of using soot and a mixture of ferrosilicium, titanium and aluminium powders at different ratios to obtain a new type of MAX phase powder with ferromagnetic properties through self-propagating high-temperature synthesis. To obtain MAX phase powder in the presence of iron and silicon for the purpose of this research, we used iron monosilicide (FeSi) obtained from iron and silicon containing waste of steel makers rather than expensive and scarce silicon. Optimal synthesis conditions have been identified for obtaining the MAX phase with the formula $(Fe,Ti)_3(Al,Si)C_2$ containing 90% of the master material, as well as the following inclusions: Fe_5Si_3, Fe_3Si, FeSi (6%); Al_3Ti, TiC and $TiSi_2$ (4%). Due to the presence of iron-rich silicides, the resultant MAX phase has magnetic properties. The advantage in this case is that both carbides and silicides of iron and titanium form at the same time.
The results of the experiment have been confirmed with the help of X-ray diffraction analysis. An advanced electron probe microanalysis has been applied to establish the exact composition of the resultant products and the distribution of silicides, aluminides and carbides of titanium and iron in the master phase, as well as their sizes and shapes.

Introduction

Modern science and technology require novel materials which would offer a variety of functionalities varying within a broad range. Spintronics, one of the most rapidly developing areas, has demand for a material that would combine the properties of MAX phase with ferromagnetic properties [1, 2].

Recently, researchers from the National University of Science and Technology “MISiS” succeeded in obtaining iron-containing magnetic MAX phase which has an amazing combination of properties combining those of metals and ceramics [3]. The authors point out that due to the presence of iron the resultant material will acquire additional magnetic properties, which will enable to create highly heat-resistant refractory coats and ultrasmall data storage devices. These products will have crystal lattices with unique laminar structure, as well as a unique combination of the most popular properties of metal and ceramics [4, 5]. Due to their properties, iron-containing magnetic MAX phases can be used for building high-performance engines or for designing damage-proof high-durability heat systems maintaining rigidity at high temperatures [5, 6]. MAX phases have high rigidity, resilience, chemical and thermal resistance, a low specific weight, and a low thermal expansion ratio. Such materials are excellent heat and electricity conductors [7–13].

We know that MAX phases stand for ternary layered compounds with the formal stoichiometry $M_{n+1}AX_n$ ($n = 1, 2, 3, ...$), where *M* — transition *d*-metal (Ti, Fe, Ni, Co, V, Cr, Mo and others); *A* — *p*-element (e.g. Si, Ga, Ge, Al, Cd, Sn and others); *X* — carbon or nitrogen [14, 15].

The authors found that MAX phases can be doped with elements that have similar properties. A few solid solutions have been synthesized in which the *M* and *A* atoms were partially substituted with atoms having similar atomic radius [16, 17]. Isomorphous substitution of one element with another changes mechanical and thermal properties of the material and can be of interest in terms of creating functional materials consisting of four and more compounds with a MAX phase structure.

MAX phases contain carbon. In such systems carbon acts as a reducing agent, and it controls the growth of iron silicide crystals for the initial stage. Carbon also helps produce gas bubbles, which are responsible for the porosity, lightness and laminar structure characteristic of MAX phases.

A particular attention should be given to the MAX phases (in particular, Ti_3SiC_2) that are mainly produced by self-propagating high-temperature synthesis (SHS) [18–22]. The advantage in this case is that both carbides and silicides of titanium form at the same time.

Titanium also plays an important role. In many SHS MAX phases it is with titanium that the process starts. Titanium interacts with soot and aluminium forming TiC and a liquid Ti–Al phase. During cooling the TiC grains dissolve in the liquid Ti–Al phase forming, for example, Ti_3AlC_2 [11].

Considering the above, substituting titanium with iron would not be justifiable. Being also a *d*-element, iron is not easily soluble in titanium (10% maximum), but because the two elements have the same diameter they can substitute each other forming solid solutions. Keeping in mind aluminides, a complete substitution of aluminium with silicon would not be reasonable either. Besides, aluminium leads to higher heat generation in the SHS production of MAX phases.

To obtain MAX phase powder in the presence of iron and silicon for the purpose of this research, we used iron monosilicide (FeSi) obtained from iron and silicon containing waste of steel makers rather than expensive and scarce silicon [23, 24]. Thus, the produced MAX phase has the following composition: $(Fe, Ti)_3(Al,Si) C_2$, where iron and titanium are used as d-elements and Si and Al — as *p*-elements. The advantage provided by this method is that iron and silicon are present in the structure of the resultant MAX phase. Due to the production of multicomponent SHS products built with carbides, aluminides and silicides of titanium and iron, which are refractory compounds, the resultant product has more layers and retains all the properties of its components.

Review of the literature suggests that the Ti_3AlC_2-based MAX phase produced by SHS, similarly to Ti_3AlC_2, should have a more layered structure and magnetic properties [19] and can find application in both powder metallurgy and microelectronics.

Problem Statement

We know that, according to the Fe–Si phase diagram [25], depending on the concentration of iron and silicon, silicides are formed rich in iron (Fe_3Si, Fe_2Si, Fe_5Si_3, FeSi) and silicon ($FeSi_2$, Fe_2Si_5), which have different applications. Iron-rich silicides, i.e. Fe_3Si and Fe_5Si_3, manifest magnetic properties even at room temperature. Some researchers believe that it is from iron monosilicides that these silicides form.

Thus, when MAX phases are produced by SHS, the presence of iron monosilicides does not contradict with the fact that iron-rich silicides can be formed that impart ferromagnetic properties to the resultant alloy.

This research aims to establish if it would be possible to obtain a new type of iron- and silicon-doped MAX phase compounds containing iron-rich silicides with the general formula $(Fe,Ti)_3(Al,Si)C_2$ on the basis of Ti_3AlC_2 from soot and a mixture of FeSi, Ti and Al powders at different ratios with the help of SHS in combustion mode. The authors also looked at how the amount of FeSi influences phase formation and examined the crystal lattice in the final MAX phase.

Materials and Methods

The following powders were used for sample production: FeSi — FS-25 (25% Si, 2 μm), carbon black (soot) of P-701 grade (99.5%, 2 μm), Ti — PTS (98% pure, average particle size 100 μm), aluminium of PA-4 grade (99%, 50 μm). The above powders were taken at certain weight ratio, placed in a porcelain mortar and thoroughly ground to the state of homogenous mass. Synthesis was carried out in a reactor at atmospheric pressure. The compositions of the synthesized samples were determined with the help of X-ray diffraction analysis (XRD). The surface morphology and structure of the samples were surveyed on a high-resolution scanning electron microscope Mira by Tescan (Czech Republic) equipped with an electron probe microanalyzer Aztec [26]. An advanced electron probe microanalysis was applied to examine the phase composition and to establish the exact composition of the resultant products in the master phase, as well as their sizes and shapes [27].

Fig. 1. Laboratory SHS reactor

The experimental production of MAX phase by SHS was carried out in a reactor, which is a steel container (**Fig. 1**) made of two parts [22, 23]. The bottom section is filled with quartz sand, while the top section has a tapered shape and is open at the top. Pockets were made in the quartz sand in the centre of the bottom section, in which sample burden was placed comprised of the initial mixtures of the stoichiometric composition. The premixed burden was placed in the quartz sand and the tapered top was placed over it. An initiator (Ti+C) was poured in the core of the sample. A hot tungsten coil was placed to the top end of the sample to initiate combustion. This initiates a chemical reaction in the surface layers creating a combustion wave which propagates at constant rate across the sample — i.e. an SHS takes place. Combustion lasts for 10–15 sec within the temperature range of 2300–2500 °C. As the combustion products cool down they form porous mass, which is then ground into metal powder.

The obtained MAX phase alloys were subjected to electron probe microanalysis and X-ray diffraction analysis (XRD).

Findings

Three different compositions with extra FeSi (10, 20 and 30%) were prepared to obtain MAX phase with the formula $(Fe, Ti)_3(Al,Si)C_2$. The initial burden was mixed to form different stoichiometric proportions of the components: 3Ti–1(Al,Si)–2C–1FeSi, 3Ti–1Al–2C–2FeSi, 3Ti–1Al–2C–3FeSi. As expected, the best result was obtained with 30% extra FeSi as the higher the FeSi concentration is, the higher the concentration of iron is and the resultant silicides have stronger magnetic properties.

Fig. 2 shows a general view of the resultant MAX phase.

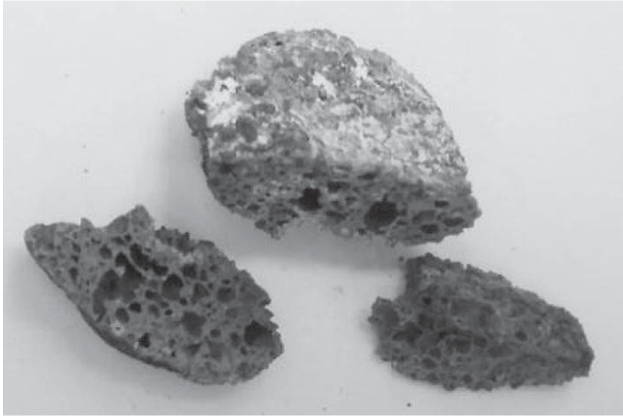
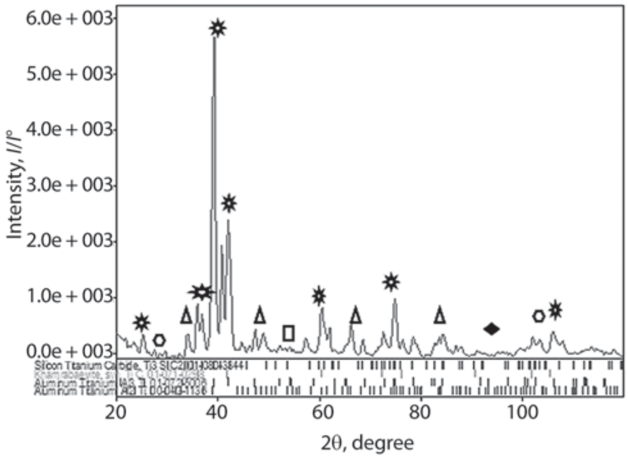


Fig. 2. MAX phase: General view



a

Resultant MAX phase composition			
Symbols and formulas of the components		Phase name	Concentration (%)
✵	$(FeTi)_3(SiAl)C_2$	Iron and titanium carbosilicide	90
Δ	Fe_3Si, Fe_3Si_2, FeS	Iron silicides	6
○	Al_3Ti	Titanium aluminide	2
□	TiC	Titanium carbide	1
◆	Ti_3Si_3	Titanium silicide	1

b

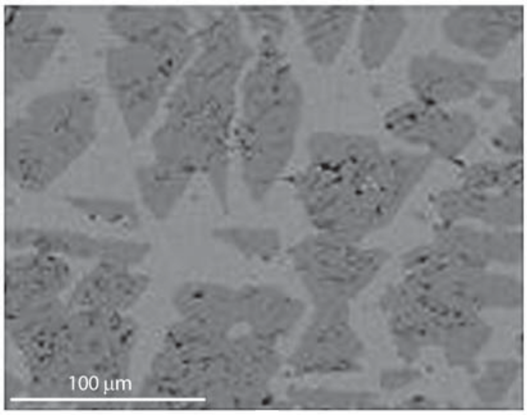
Fig. 3. Radiographs of the SHS products with extra 30% of FeSi to the stoichiometric composition (*a*) and the composition of the obtained MAX phase (*b*)

With the help of SHS, alloys were produced from the above mentioned mixtures, which were then used in experiments and a series of analyses was carried out with them.

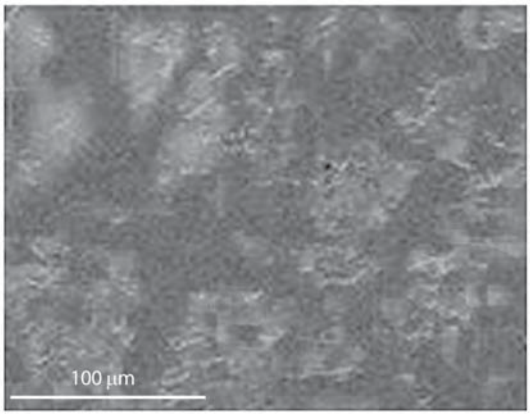
Below you will find the results of the X-ray diffraction analysis (*a*) and the composition (*b*) of the resultant product.

The experimental data show that, besides the master phase $(Fe,Ti)_3(Al,Si)C_2$, the synthesized products have highs that are characteristic of titanium carbides and silicides (~10–15 vol.%) (**Fig. 3 *a, b***).

The XRD analysis showed that the final product comprises multiple phases and, besides the master phase, contains crystals of Fe_3Si, Fe_5Si_3, FeSi responsible for the magnetic properties of the master phase, as well as the phases of Al_3Ti, Ti_5Si_3 and TiC (**Fig. 3, *b***).



a



b

Fig. 4. Phase composition (*a*) and microphotograph (*b*) of the resultant product, ×500

Fig. 4 shows the results of the electron probe microanalysis based on the map of the resultant metallic phase. The figure shows a non-uniform distribution of phases in both the master phase grains (**Fig. 4, *a***) and the microphotographs made with a scanning microscope (**Fig. 4, *b***).

As can be seen from the figure, the metallic phase is comprised of the master phase. At the same time, there are black points visible that are typically indicative of iron silicides. When iron sulphide phases interact during homogenization, two or more solid solutions form which have a random structure of the $(Fe,Ti)_3(Al,Si)C_2$ type. The grains of these phases, which have an average size of about 25–50 μm, retain clear-cut boundaries. The phase impurities enriched with iron silicides concentrate predominantly at grain boundaries.

An advanced electron probe microanalysis was applied to establish the exact composition of the resultant products and the size distribution of silicides, aluminides and carbides of titanium and iron in the master phase [26, 27]. The analysis follows the following sequence (**Fig. 5, *a–c***). Three spectrums were captured in our case. **Table 1** describes the chemical composition of separate spectrums.

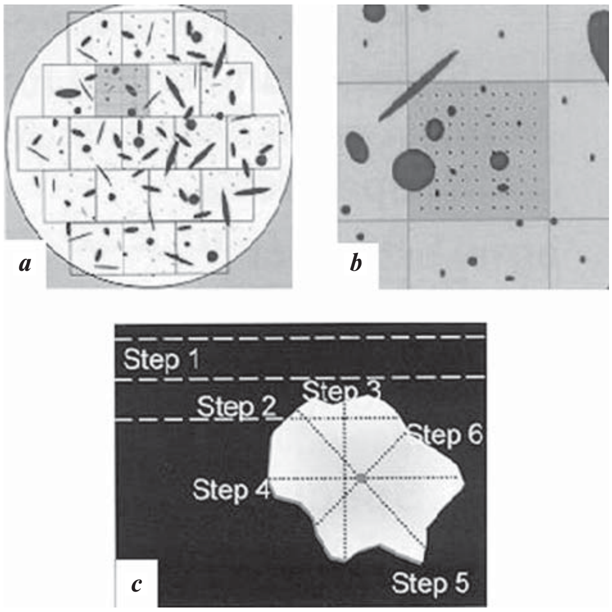


Fig. 5. Automatic analysis of impurities:
a — image break-down; *b* — electron beam travelling across the field in the array;
c — determine the sizes of the particles detected by back-scattering electrons, focus the beam on each particle and analyze the composition with the help of electron probe microanalysis

Table 1. **Overall elemental composition, Wt.%**

Spectrum	Al	Si	Ti	C	Fe
Spectrum 1	0.54	22.65	7.68	1.18	67.95
Spectrum 2	0.46	22.84	6.85	1.33	68.52
Spectrum 3	0.38	22.82	6.76	0.93	68.95
Average	0.46	22.82	7.04	0.81	68.47

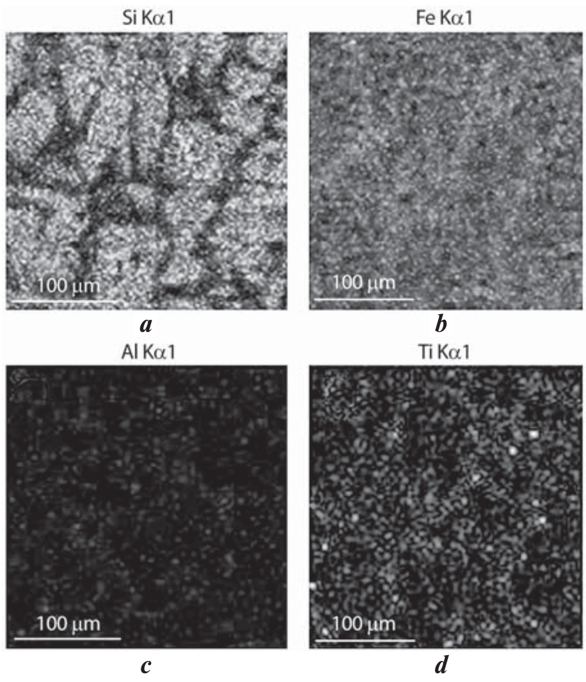


Fig. 6. SHS product analysis results:
a–d — map-based electron probe microanalysis

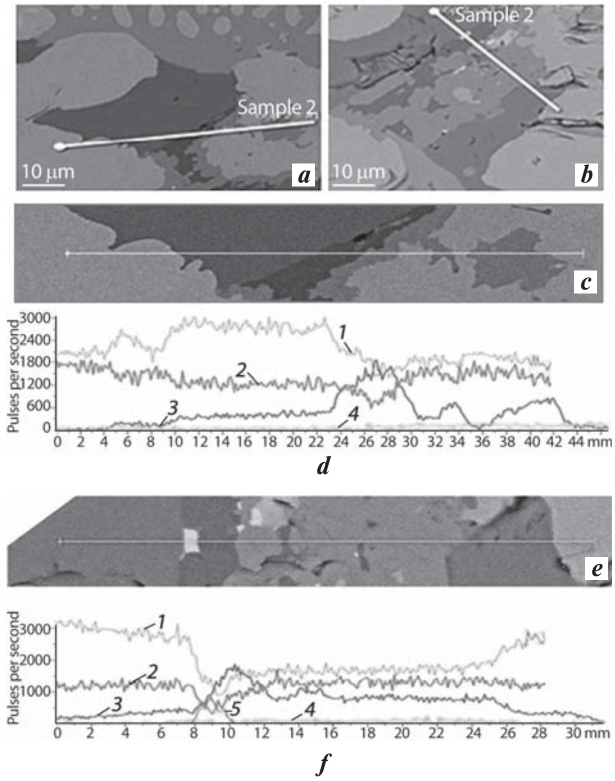


Fig. 7. Electron probe microanalysis results by line for Sample 2:
1 — FeK-series; *2* — TiK-series; *3* — SiK-series; *4* — AlK-sries; *5* — MnK-series

Table 1 shows a noticeable drop in the amount of aluminium. It happens because some of the aluminium transfers into slag in the form of aluminates. Aluminium does not react with silicon. Titanium is poorly soluble in iron (the solubility of titanium in α-Fe does not exceed 9.8 at.%). But as titanium and iron have almost the same radii, they substitute each other in the MAX phase crystal lattice. Some of the carbon binds with titanium forming carbides.

Fig. 6, *a* and ***d*** show the distribution of separate elements in the MAX phase. As can be seen from these pictures, the distribution of separate elements in the alloy is also non-uniform. The dominant elements include silicon, iron and titanium. There is not much aluminium (**Fig. 6, *c***), which is probably due to its transition into slag. The variants of the chemical composition were visually analyzed. Pixels with the spectrums (of the same composition) are marked with the same colour.

Fig. 7, *a* and ***b*** show a concentration profile reflecting the distribution of elements along the lines *1* (*a*) and *2* (*b*) for Sample 2.

The results of electron probe microanalysis indicate that the main phases include iron, silicon and titanium (**Fig. 7, *c*** and ***d***). According to the quantitative X-ray diffraction analysis, the sample has a minimum concentration of titanium carbide (TiC). 5% of $TiSi_2$ is also detected but these compounds are not captured in the X-ray pictures (see **Fig. 3**) or in the pictures (**Fig. 7, *d*** and ***f***).

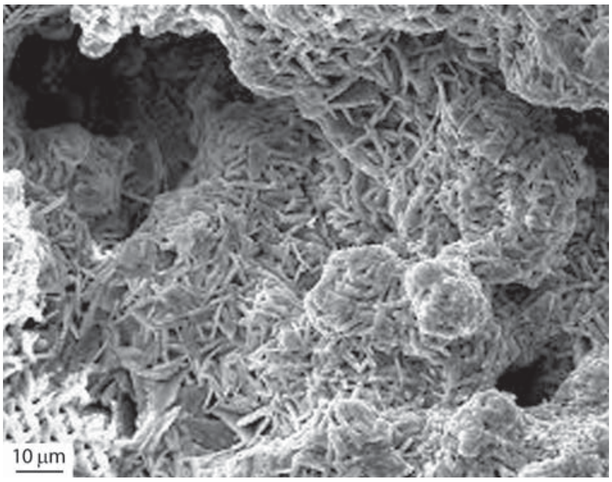


Fig. 8. Surface structure (×1000) of the SHS product of the system Ti–Fe–Si–Al–C

Along Line *1* (**Fig. 7, *a*, *c* and *d***) the spaces of 0–9 µm particles are in the homogenous phase. However, the concentration profiles show (**Fig. 7, *d***) that the curves often change as various new phases form. The spaces of 9–21 µm particles occupy a large area that looks like an iron silicide region (Fe_5Si_3), which can be found again from 34–40 µm. The 24–30 µm spaces house new formations stretching for 34–42 µm. These silicides are in the homogenous MAX phase. Black points can be seen in a few spots at the top of the line that look like various types of carbides and silicides of titanium and aluminium. It can probably be attributed to transitions of various forms of iron-rich silicides (Fe_5Si_3, Fe_3Si, FeSi) (**Fig. 7, *a*, *c* and *d***).

Along Line *2* (**Fig. 7, *b*, *e* and *f***) the spaces of particles of up to 8 µm are in the homogenous phase. A new square-shaped phase forms in the space of 8–9 µm particles. This phase looks like impurities of titanium carbide (TiC) or titanium silicide ($TiSi_2$). The spaces of 9–11 µm particles can be characterized with changing phases. This conglomerate looks like iron silicide (Fe_5Si_3). The space of 11–14 µm particles looks like a new phase being formed, which has a round shape and looks like another iron silicide (Fe_3Si). The space of the 16–25 and 28–30 µm particles constitute the main MAX phase. The phase between them, which looks like a 0–8 µm phase, is also homogenous.

Discussion

A study has been carried out for obtaining a MAX phase on the basis of the titanium carboaluminide (T_3AlC_2) lattice by SHS by substituting a part of titanium atoms with iron atoms and a part of aluminium atoms with silicon atoms in the initial burden.

The experimental data suggest the possibility of obtaining a new type of MAX phase with the formula $(Fe,Ti)_3(Al,Si)C_2$ from a mixed powder of FeSi, Ti, Al and soot using different combinations of Ti–Al–C by SHS in combustion mode. The authors also looked at how the amount of FeSi influences phase formation and examined the crystal lattice in the final MAX phase.

The study showed that when the MAX phase cools down it turns into a laminar, porous and light material with a high level of stability (**Fig. 8**). Grinding turns the MAX phase into powder, which is a composite material designed for powder metallurgy. Due to the presence of iron and silicon, the resultant product has more phases and retains all the properties of composite materials as, besides iron and titanium carbides, it also contains silicides of the same metals.

The X-ray diffraction analysis data confirmed the results of the electron probe microanalysis. The produced master MAX phase is mixed with other phases, i.e. it is of heterogenous nature. In the mainly homogenous mass there can be found inclusions of silicides, aluminides and carbides of titanium and iron, which is also confirmed by the X-ray diffraction analysis data (see **Fig. 3**). A quantitative analysis of material from three separate experiments, which used structural data, showed that the inclusions accounted for 10 Wt.% while the master phase accounted for 90 Wt.%. These figures are so far maximum compared with the results obtained by other authors [9, 10, 17, 28]. Moreover, our MAX phase has more components as, apart from aluminides, silicides and carbides of titanium, it contains similar compounds with iron. Aluminides, silicides and carbides of iron contribute to the laminar structure of MAX phases [28].

The main crystallographic characteristics of the synthesized $(Fe,Ti)_3AlSiC_2$ phase have been determined. It was found that the above phase belongs to hexagonal syngony and is presented by a solid solution in which the Ti and Fe atoms are disordered in the carbon layer having equal positions in the structure. Due to the presence of iron rich silicides the resultant MAX phase has magnetic properties. The synthesized MAX phase is ground to obtain the respective powder product.

Conclusion

The findings show that the proposed SHS method can be used to produce a $(Fe,Ti)_3AlSiC_2$ MAX phase with the concentration of the master phase being 90 Wt.%.

Hence, it can be claimed that, in terms of the key component of MAX phases, our findings exceed the data reported by Russian (approximately 75%) [10, 28] and foreign authors (approximately 80%) [9, 17]. We believe that by changing the amounts of the components an even higher concentration of the MAX phase can be achieved in the final product, and magnetic properties of the produced materials can be studied. We hope that our colleagues from Belorussia will follow the Armenian-Belorussian contract AB 16/48 and use our metallic powders for parts manufacturing at the research and production division of the Institute for Powder Metallurgy.

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